REMARKS

Applicants have elected the Group I claims with traverse, as discussed in the May 26, 1999 Response. In addition, in view of the outstanding requirement Under 35 U.S.C. 121 to elect a single species for prosecution, applicants elect zinc pyrithione. The structure of pyrithione is more fully delineated at page 2, lines 21-23 of the instant specification. In addition, the pyrithione structure is shown pictorially at column 1, line 25 of U.S. Patent 2,809,971 (copy attached).

No fee is believed to be due for filing this Response. However, if there are any other fees due in connection with the filing of this response, please charge them to Wiggin & Dana's Deposit Account No. 23-1665.

Respectfully submitted

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HEAVY-METAL DERIVATIVES OF 1-HYDROXY-2-PYRIDINETHIONES AND METHOD OF PREPARING SAME

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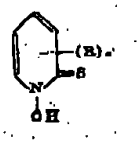
No Drawing. Application November 22, 1955, Serial No. 548,545

8 Claims. (Cl. 260—270)

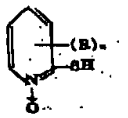
This application is a continuation-in-part of our parent application, Serial No. 358,542, filed May 29, 1953, now abandoned.

This invention relates to, and has for its object, the provision of: (A) heavy-metal salts of 1-hydroxy-2(1H)-pyridinethiones (hereinafter referred to for brevity as 1-hydroxy-2-pyridinethiones) of the general Formula I:



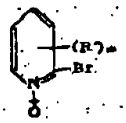
wherein R is hydrogen, lower alkyl, lower alkoxy or halogen, and *n* is a positive integer less than five; and (B) methods of preparing same.

The compounds of this invention can be prepared by a method which comprises interacting a 1-hydroxy-2-pyridinethione of the Formula I, preferably in the form of a soluble salt thereof (e. g. an alkali metal salt or ammonium salt thereof), with a soluble compound of the desired heavy-metal (II) in a solvent for the reactants, and recovering the reaction product. (Reactant I may be in tautomeric equilibrium with the corresponding 2-mercaptopyridine-1-oxide, i. e.:



This tautomerism will not be alluded to hereinafter, it being understood that such tautomeric form (e. g., 2-mercaptopyridine-1-oxide) is included when referring to the compounds of this invention either by formula such as I, or by a name such as 1-hydroxy-2-pyridinethione.)

Examples of utilizable compounds I include the following (inter alia) and soluble salts thereof: 1-hydroxy-2-pyridinethione; 1-hydroxy-3(4,5, or 6)-methyl-2-pyridinethione; 1-hydroxy-3(4, 5, or 6)-ethyl-2-pyridinethione; 1-hydroxy-3(4, 5, or 6)-n-butyl-2-pyridinethione; 1-hydroxy-3(4, 5, or 6)-methoxy-2-pyridinethione; 1-hydroxy-3(4, 5, or 6)-ethoxy-2-pyridinethione; 1-hydroxy-3(or 5)-bromo-2-pyridinethione; 1-hydroxy-3(or 5)-chloro-2-pyridinethione; 1-hydroxy-4,6(or 3,6 or 5,6)-dimethyl-2-pyridinethione; 1-hydroxy-4,6(or 3,6 or 5,6)-diethyl-2-pyridinethione; 1-hydroxy-2(4, 5, or 6)-ethyl-6(3,4 or 5)-methyl-2-pyridinethione; 1-hydroxy-4,5(or 3,6 or 5,6)-dimethoxy-2-pyridinethione; 1-hydroxy-3,5-dibromo-2-pyridinethione; 1-hydroxy-3,5-dichloro-2-pyridinethione; 1-hydroxy-4,5,6-trimethyl-2-pyridinethione; and 1-hydroxy-3,4,5,6-tetramethyl-2-pyridinethione. The unsubstituted 1-hydroxy-2-pyridinethione and the monosubstituted 1-hydroxy-2-pyridinethione are known compounds which can be prepared as disclosed in J. A. C. S. 72, 4362 (1950). The polysubstituted 1-hydroxy-2-pyridinethiones are new compounds which can be prepared by a method comprising reacting the desired 2-amino-polysubstituted-pyridine with hydrobromic acid and bromine and reacting the product thus formed with nitrous acid to yield the corresponding 2-bromo-polysubstituted-pyridine, introducing the 1-oxide group by treatment with a peracid, such as perbenzoic or peracetic acid to form the corresponding 2-bromo-polysubstituted-pyridine-1-oxide of the Formula III:



wherein R' is lower alkyl, lower alkoxy, or halogen and *m* is a positive integer from two through four.

To prepare the 1-hydroxy-polysubstituted-2-pyridinethiones, utilizable as starting materials in the preparation of the heavy-metal salts of this invention, the compounds of Formula III are reacted with an alkali metal sulfide, an alkali metal hydrosulfide or preferably thiourea. If thiourea is used, the reaction is optimally conducted in an organic solvent, such as alcohol, at an elevated temperature, and the resulting product is converted to its alkali metal or ammonium salt by alkalization with a base such as an alkali metal hydroxide or ammonium hydroxide or a salt of the alkali metal with a weak acid (e. g. sodium carbonate). The reaction yields an alkali metal or ammonium salt of a compound of Formula I, wherein *n* is 2, 3, or 4, depending on the degree of substitution of the starting pyridine reactant.

Suitable heavy-metal compound reactants (II) utilizable in the conversion of compounds of Formula I (or their alkali metal or ammonium salts) to the heavy-metal salts of this invention include salts in which the heavy-metal group is (inter alia) copper, iron, manganese, tin, mercury, cobalt, chromium, lead, gold, cadmium, nickel, silver, zinc, titanium, arsenic, antimony, and bismuth (the term heavy-metal, as employed herein, including the heavy non-metals of metallic character, such as arsenic). The reactants II may be (inter alia) nitrates, acetates, sulfates, and halides. When a semi-metal such as arsenic, antimony, or bismuth, is used, in some instances less than the total valence of the element is used in the making of the heavy-metal salt, so that a basic salt is produced as illustrated in Example 9, hereinafter.

The following examples are illustrative of, but not limitative of, the invention:

EXAMPLE 1

Manganese salt of 1-hydroxy-2-pyridinethione

A solution of 0.99 g. (0.005 mole) of manganese chloride tetrahydrate in 50 cc. of water is added to a solution of 1.27 g. (0.01 mole) of 1-hydroxy-2-pyridinethione in 10 cc. of N sodium hydroxide. The product, a yellow solid, precipitates immediately, and is filtered, washed with water, alcohol and ether, and is air-dried. Weight about 1.3 g.

EXAMPLE 2

Nickel salt of 1-hydrogen-2-pyridinethione

A solution of 1.18 g. (0.005 mole) of nickel chloride hexahydrate in 50 cc. of water is added to a solution of